INFLUENCE OF CARBON AND NITROGEN IMPURITIES ON THE CORROSION OF
STRUCTURAL MATERIALS IN A FLOWING LITHIUM ENVIRONMENT*

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Received 11/1/88
FEB 24 1989

September 1988

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CONF-881031--65

DE89 007398

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To be presented at the Eighth Topical Meeting on the Technology of Fusion Energy, Salt Lake City, Utah, October 9-13, 1988.

*Work supported by the U. S. Department of Energy, Office of Fusion Energy, under Contract W-31-109-Eng-38.

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INFLUENCE OF CARBON AND NITROGEN IMPURITIES ON THE CORROSION OF STRUCTURAL MATERIALS IN A FLOWING-LITHIUM ENVIRONMENT

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ABSTRACT

Chemical interactions involving nonmetallic elements play a dominant role in the corrosion behavior of ferrous and vanadium base alloys in lithium. Metallographic evaluations of the surface morphology and compositional changes of lithium-exposed ferrous and vanadium alloys are presented. Data on the corrosion behavior of several ferritic, austenitic, and vanadium-based structural materials in flowing lithium are reviewed and the effects of nonmetallic elements on corrosion are discussed.

I. INTRODUCTION

Liquid lithium (Li) is a leading candidate as a tritium breeder material for fusion reactors because of its acceptable tritium-breeding and efficient heat transfer characteristics. The self-cooled blanket concept is particularly attractive because of the inherent simplicity of using Li as both a breeder and coolant. However, the compatibility of liquid Li with the containment materials is a major concern. Data from an investigation of the corrosion behavior of candidate structural materials in flowing Li loops¹ indicate that mass transfer and deposition of corrosion products may determine the maximum operating temperature in some liquid-metal blanket systems.

In flowing Li systems, the corrosion rates of ferritic and austenitic steels reach a steady-state value after an initial transient period characterized by rapid dissolution. The steady-state corrosion rates for ferritic steels increase with an increase in temperature whereas the corrosion rates of austenitic steels are insensitive to temperature in the range from 370 to 550° C.¹ The initial dissolution stage is associated with rapid changes in surface composition and the alloy surfaces develop a dimpled appearance. The austenitic steels form a

ferrite layer due to depletion of nickel from the steel. Both ferritic and austenitic steels show depletion of chromium (Cr). The ferritic steels show greater resistance to corrosion than the austenitic stainless steel (SS).

The corrosion data indicate that dissolution of major alloy elements and mass transfer as well as chemical interactions between alloy elements and nonmetallic elements such as nitrogen (N) and carbon (C), influence the overall corrosion behavior of ferrous alloys.^{1,2} An increase in the N content of the Li increases the weight losses for ferritic and austenitic steels. The formation of a ternary nitride Li_9CrN_5 has been observed on steel specimens exposed to Li at temperatures between 400 and 600° C.^{1,3-5} Mixed iron-chromium carbide M_{23}C_6 has also been detected on austenitic stainless steel exposed to C-contaminated Li.^{4,5}

Chemical interactions also play a dominant role in the corrosion behavior of vanadium (V) alloys.⁶ Alloys containing various amounts of Cr and titanium (Ti) pick up N and C when exposed to Li that contains 20 to 50 wppm N and 8 to 12 wppm C at temperatures between 370 and 540° C. Alloys containing 15 to 20% Ti show the lowest corrosion while pure V exhibits the highest corrosion rate.

This paper presents data on the surface morphology and compositional changes of Li-exposed ferrous and V alloys. Data on the corrosion behavior of several ferritic, austenitic, and V-based structural materials in flowing Li are reviewed and the effects of nonmetallic elements on corrosion are discussed.

II. EXPERIMENTAL PROCEDURE

Corrosion tests were conducted in a forced-circulation Li loop equipped with cold- and hot-trapping purification capabilities to control the concentration of nonmetallic elements. A detailed description of the loop and the test procedure has been presented previously.⁷ The exposure temperature and time, Li loop operating conditions, and the N content of the Li, are given in Table 1. For all tests, Li was circulated at ~ 1 l/min in the primary loop, and the concentrations of C and hydrogen (H) in the Li were ~ 10 and 120 wppm, respectively.

After exposure to Li, the specimens were cleaned in alcohol and water. Several specimens were analyzed chemically to determine the changes in the concentration of nonmetallic elements; the surface reaction products were analyzed by x-ray diffraction.

III. RESULTS

A. Ferritic and Austenitic Steels

The data for weight losses and steady-state dissolution rates of HT-9, Fe-9Cr-1Mo, and Type 316 SS reported elsewhere^{1,7,8}, show that, for all alloys, an increase in the N content of the Li from 20 to 100 wppm increases the weight loss during the initial transient period.¹

Nitrogen can react with alloy elements and Li to form stable ternary nitrides and thus accelerate the corrosion of ferrous alloys.^{4,9} The equilibrium concentrations of N and C in Li for which metal nitrides and carbides are stable^{5,10,11} are shown in Fig. 1. The ternary nitrides are soluble in alcohol or water and, therefore, are not observed on clean specimens. The presence of ternary nitride Li_9CrN_5 on HT-9 and Type 316 SS specimens exposed during Run 6 was detected by chemical analysis of the methanol used for cleaning the specimens.¹ The concentrations of the major elements (expressed as wppm in Li) that were dissolved in the methanol are given in Table 2. The high concentration of Cr in the solutions indicates the formation of the ternary nitride of Cr on the alloy surfaces exposed to Li. The Cr content of the methanol solution after cleaning Type 316 SS specimens was significantly greater than the Cr content of the methanol after cleaning HT-9 specimens. This was particularly true for specimens exposed at 482° C. The relatively high concentrations of molybdenum (Mo) in the solutions after cleaning Type 316 SS specimens also indicate the presence of ternary nitrides involving Mo. These results indicate that chemical interactions between alloy elements and N play a dominant role in the corrosion behavior of austenitic steels in Li. The effect of these interactions on the corrosion behavior will be larger at lower temperatures, eg., at 482 or 427° C, because the driving force for nitride formation increases as temperature decreases.

An implication of such chemical interactions is that the corrosion behavior can not be accurately obtained from a single specimen exposed for various times; particularly for Type 316 SS. The formation of ternary nitrides during each exposure period and the subsequent loss during the cleaning procedure results in greater weight loss and corrosion rate. The relatively constant dissolution rates obtained for Type 316 SS ($\sim 2 \text{ mg/m}^2\text{.h}$) at temperatures between 372 and 538° C may be attributed to chemical interactions involving N and the experimental procedure. Separate specimens should be exposed to Li for different times to accurately establish the dissolution rates of Type 316 SS. Figure 1 indicates that the N

content of the Li should be below ~ 1 wppm to avoid formation of ternary nitrides and their effects on corrosion.

The corrosion data from the various test runs indicate large deposits on specimen surfaces^{1,7} (for example, see Fig. 2). A detailed examination of the Li-exposed specimens reveals surface deposits on all specimens exposed at 427 or 482° C. Specimens exposed at the downstream location contain very large particles whereas the specimens exposed at the maximum loop temperature contain fine surface deposits. Significantly fewer deposits are seen on HT-9 and Fe-9Cr-1Mo specimens than on Type 316 SS specimens. X-ray analyses indicate that these deposits are carbides and that the nature of the carbides changes with exposure time. For example, $M_{23}C_6$ carbides are observed after relatively short exposure times (~ 1000 h at 427 or 482° C) whereas both $M_{23}C_6$ and M_7C_3 are observed after longer exposure times (> 2500 h). The total carbon content of the specimens, however, did not increase significantly with an increase in time from 1000 to 5000 h.

Surface deposits have also been observed on pure Cr specimens exposed to Li at 482 and 427° C.⁸ The deposits were identified as $Cr_{23}C_6$ for the specimen exposed at 482° C (maximum loop temperature) and $Cr_{23}C_6$ and Cr_7C_3 for the specimen exposed at 427° C (downstream location).

The ferritic and austenitic steels exposed to Li during Runs 4,5, and 6 were analyzed chemically to determine the changes in C content. The results are plotted in Fig. 3. Some specimens were mechanically polished to remove the surface deposits or the ferrite layer on Type 316 SS before the bulk C concentration was measured. The results for Type 316 SS indicate that the material decarburizes at 538° C and carburizes at 482 and 427° C; little or no change was observed at 372° C. The influence of surface deposits is significant only for the specimens exposed at the downstream location, viz., the bulk C content of these specimens is $\sim 22\%$ lower than that of the unpolished specimen. The presence of large surface deposits on the downstream specimens is most likely due to the deposition of Cr from Li. The decarburization/carburization behavior of Type 316 SS does not seem to be affected by the surface deposits. Specimens exposed at the maximum loop temperature of 482° C have little or no deposits but contain higher C concentrations (737 wppm) than the specimens exposed at the same temperature but at the downstream location (652 wppm), which have surface deposits. The formation of ternary nitrides may, however, influence the C transfer. The lack of C transfer even after an ~ 5000 -h exposure to Li at 372° C may be attributed to kinetic limitations and possibly the presence of ternary nitrides on the specimen surface.

The results for HT-9 and Fe-9Cr-1Mo, Fig. 3b, indicate no C transfer after long exposure at temperatures between 372 and 538° C. The slightly higher C content of specimens exposed at 482 and 427° C appears to be associated with the surface deposits.

These results indicate that chemical interactions involving C are not likely to influence the overall corrosion behavior of ferrous alloys significantly. The carbides that form on the alloy surfaces are adherent. The transfer of C to and from the alloys, and the carbide deposits on the surface, may, however, influence the weight change measurements. For example, a 300 wppm increase in bulk C content in the foil specimens used in this investigation would correspond to an increase of ~ 0.35 g/m² in weight. Such weight changes will be insignificant for the austenitic Type 316 SS which shows 10- to 30- g/m² weight loss after the initial transient weight loss period. The ferritic steels show no change in the bulk C content.

B. Vanadium Alloys

The corrosion data for several V alloys⁶ exposed at 482° C to Li containing ~ 10 wppm C and 20 to 50 wppm N indicate that the dissolution rates decreased in the following order: pure V > V-3Ti-1Si > V-5Ti-(12-15Cr) > V-(10-15Cr)-(3Fe-1Zr) > V-(15-20Ti)-7.5Cr. All alloys picked up N and C and lost oxygen (O). The low dissolution rates for the alloys containing ≥ 15 % Ti are due to the formation of a continuous surface scale. Alloys containing < 5 Ti % do not develop a uniform surface scale and exhibit higher corrosion rates. The addition of Cr to V seems to influence the chemical interactions and decrease the corrosion rates.

The concentrations of N and C in pure V and some alloys exposed to Li at temperatures between 427 and 538° C are given in Table 3. At 538, 482, and 427° C, the solubility of N in pure V is 4670, 3570, and 2640 wppm, respectively; that of C is 487, 366, and 265 wppm, respectively.¹⁰ For pure V specimens, the measured N content is slightly below the solubility level and the C content represents the saturation level. Figure 1 indicates that VN is not stable at 482° C in Li containing 20 wppm N (conditions for Run 8). The partitioning of N between pure V and Li can be obtained from the equilibrium distribution coefficient K_w ^{10,11} given by

$$K_w = C_v / C_L = \exp (6.52 - 1394 / T)$$

where C_V and C_L are the concentrations (weight units) of N in V and Li, respectively, and T is absolute temperature. For 20 wppm N in Li, the equilibrium N content in V should be 2140 and 1840 wppm at 482 and 427° C, respectively. The measured N concentration in pure V exposed at 482° C is close to the equilibrium concentration. The equilibrium value is not achieved after ~ 1400 h at 427° C due to kinetic limitations.

These results indicate that the relatively high corrosion rates for pure V can not be attributed to chemical interactions to form nitrides. Figure 1 shows that V_2C is stable under the present exposure conditions, i.e., 10 wppm C in Li. X-ray analyses of the pure V specimens, however, did not show any carbides or nitrides on the specimen surfaces. It is likely that the V_2C which forms on pure V specimens is not adherent and spalls during Li exposure. This may be the dominant contribution to the weight loss of V alloys.

The V alloys show an increase in N and C content. The gain in N increases with time and temperature. Analyses of the specimens with or without the surface scale indicate a significant increase in N content of the bulk material, a finding that is confirmed by hardness measurements which showed an increase in microhardness of the surface region of the specimens.⁶ However, x-ray analyses of these specimens did not show the formation of metal nitrides or carbides; only broadening of the x-ray peaks corresponding to the base material were observed. In most specimens, N is in solution. However, the specimens with > 1 wt% N were consumed in the chemical analyses and thus were not available for x-ray analysis.

The N-rich scale on the V alloys is quite hard and brittle and can break off under thermal stresses, resulting in higher weight losses. Spalling of the surface scale was, however, rare. The corrosion mechanisms for V alloys are most likely dissolution of alloy elements and chemical interactions involving C. Chemical interactions with N have a secondary effect, but may be more important for the effects on mechanical properties.

IV. CONCLUSIONS

(a) The dissolution of major alloy elements, as well as chemical interactions between N and Cr or Mo, control the corrosion behavior of ferrous alloys. The contribution of chemical interactions is significant for austenitic Type 316 SS. Thermodynamic data indicate that the N content in Li should be < 1 wppm to avoid chemical interactions.

(b) The weight loss data for Type 316 SS obtained from a single specimen exposed for various times do not accurately represent the corrosion rates. The relatively constant dissolution rates reported for Type 316 SS at temperatures between 372 and 538° C are most likely due to the experimental procedure and contributions of chemical interactions.

(c) When exposed to Li containing ~ 10 wppm C, the austenitic Type 316 SS decarburizes at 538° C and carburizes slightly at 482 and 427° C. The ferritic HT-9 and Fe-9Cr-1Mo steels are resistant to decarburization/carburization and show little or no C transfer.

(d) Carbon deposits are observed on the ferritic and austenitic steel surfaces, particularly on specimens located at the downstream position. Carbon transfer does not appear to affect the dissolution behavior of ferrous alloys.

(e) The V alloys pick up N and carbon from Li. Alloys with Ti or Cr develop a N-rich surface layer.

(f) Chemical interactions involving C play an important role in the dissolution behavior of V alloys.

VI. ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Fusion Energy, under contract No. W-31-109-Eng-38. Collette Marsh performed the carbon analyses and Urs Geiser helped with the XRD work.

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Table 1. Lithium Loop Operating Conditions for Various Corrosion Tests

Test Run	Loop Temperature (°C)				N content of the Li (wppm)	Exposure Time (h)	
	Test Vessel	Exp. ^a Vessel	Supply Vessel	Cold Trap		Test Vessel	Exp. Vessel
1	482	482	432	212	< 50	1295	5000
2	482 ^b	482	407	230 ^c	~ 250	---	1997
3	427	482	407	230	~ 100	1100	---
4	482	427	410	212	< 100	5521	6501
5	427	372	372	206	~ 100	5023	4955
6	538	482	410	208	~ 50	3655	3330
8	482	427	426	213	~ 20	2158	2062

^a Lithium flow was from the test vessel to the specimen exposure vessel.

^b Test vessel temperature changed from 482 to 427°C after 1540 h.

^c No flow occurred through cold trap after 890 h due to plugging. Plugged sections were replaced and flow started after an additional 480 h.

Table 2. Concentrations (wppm) of Alloy Constituents in Lithium^a from Spectrochemical Analysis of Methanol Used for Cleaning Corrosion Specimens Exposed to the Lithium at 538 and 482° C

Alloy	Major Elements (ppm)							
	538° C				482° C			
	Cr	Fe	Ni	Mo	Cr	Fe	Ni	Mo
HT-9	19	67	<15	10	42	33	<15	12
Type 316 SS	46	68	13	135	207	31	14	60
Lithium ^b	<5	17	13	<10	<5	18	<15	<10

^a Lithium film which adheres to the specimen when it is removed from the loop

^b Concentration of alloying element in the loop lithium

Table 3. Carbon and Nitrogen Contents in Vanadium Alloys Exposed to Lithium

Alloy	Test Run	Exposure Condition		Impurity Content ^a (wppm)	
		Temp (°C)	Time (h)	Carbon	Nitrogen
Pure V	Unexposed			360	161 ± 41
	8	482	484	340 (330)	681 ± 65
	8	482	1508	270	3404 ± 187 (3410±129)
	8	427	1405	320	565 ± 71
V-10Cr-3Fe-Zr	Unexposed			890	271 ± 66
	6	538	590	1190	12418 ± 621(6258±227)
	8	482	1080	1070	
	6	482	687	990	4570 ± 250
V-15Cr-5Ti ^b	Unexposed			390	527 ± 109
	6	482	619	530	
	8	482	1992	570	2361 ± 114 (1955±78)
	8	427	1405	500	607 ± 84
V-15Cr-5Ti ^c	Unexposed			390	299 ± 68
	6	538	794	—	(4895 ± 179)
	6	538	1384	(670)	11935 ± 434(10022±505)
	6	482	1618	700	2808 ± 177
V-20Ti	Unexposed			—	566 ± 168
	6	538	1384	—	8862 ± 328 (5735±295)
	6	482	619	—	604 ± 124
	6	482	1618	—	(2595 ± 110)

^a Values within brackets represent concentrations for specimens which were mechanically polished to remove the surface reaction products.

^b Cam heat

^c ANL heat

VIII. FIGURE CAPTIONS

Figure 1. Equilibrium Values of Nitrogen and Carbon Concentration in Lithium for which Metal Nitrides and Carbides are Stable

Figure 2. Examples of Surface Deposits on HT-9 and Type 316 SS

Figure 3. Effect of Lithium Exposure on Carbon Concentration in (a) Austenitic and (b) Ferritic Steels

HT-9 ALLOY (Run 6)

482°C , 2528 H

TYPE 316 SS (Run 6)

482°C , 3330 H